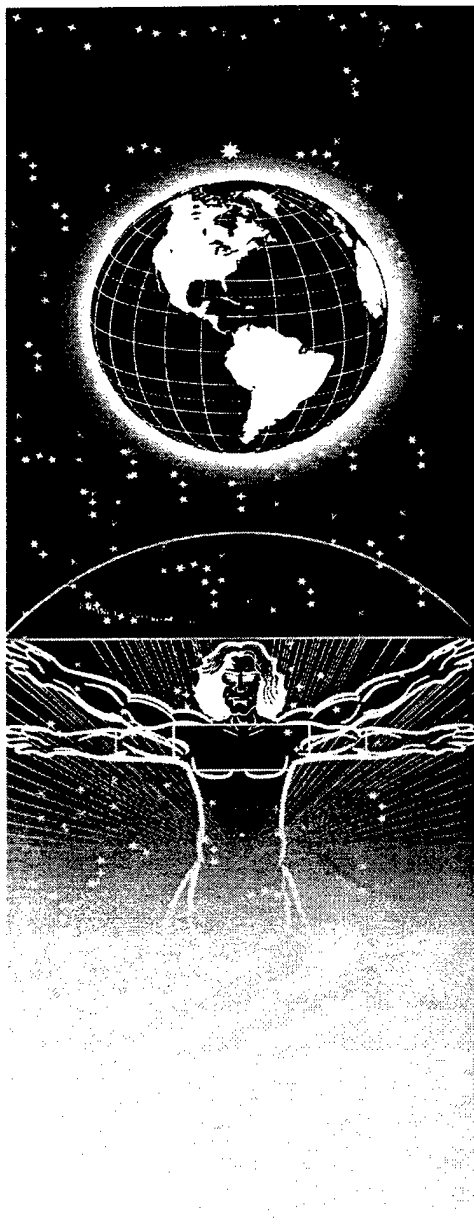AL/EQ-TR-1996-0049

UNITED STATES AIR FORCE
ARMSTRONG LABORATORY

Sorption of Humic Acids onto Aquifer Solids

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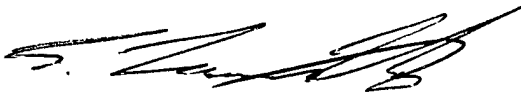Tyndall Air Force Base FL
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This technical report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service, where it will be available to the general public, including foreign nationals.

This report has been reviewed and is approved for publication.

FOR THE COMMANDER:

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14. Abstract

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PREFACE

This report was prepared as part of the Air Force Office of Scientific Research Summer Faculty Research Program sponsored by Armstrong Laboratory's Environics Directorate, Tyndall Air Force Base, Florida 32403.

The report covers research performed by Michael J. Piana, Graduate Student at Washington State University, between June and August 1988. The report is being reprinted and sent to Defense Technical Information Center because of its interest to the DOD and worldwide scientific and engineering communities. The AL/EQ mentor was Dr. E. Laurance Libelo. The AL/EQ Summer Faculty Coordinator was Ms. Mary Reynolds.

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THE SORPTION OF HUMIC ACIDS ONTO AQUIFER MATERIAL SOLIDS

Michael J. Piana

Introduction

The dark colors observed in many soils, sediments, and natural waters are the characteristic of humic substances. Humic substances are compounds formed from the biological degradation of plant and animal residue and from the synthetic activities of microorganisms. Humic materials are some of the most powerful metal-binding agents among natural organic substances and can form water-soluble and insoluble complexes with metal ions and hydrous oxides (Tipping, 1981). The structure of humic substances are extremely complex, humic materials are high molecular weight (1000-500,000 daltons) compounds comprised of numerous polyfunctional groups. including; carboxyl, phenolic, alcoholic hydroxyl, quinone and ketonic carbonyl, amino, and sulfhydryl groups. As a result of their large size and chemical complexity, humic materials have been compared to biomolecules in structure and properties. However, in contrast to biomolecules, humics are quite complex and can differ structurally from one molecule to the next. Sposito (1984) summarized the principle characteristics of humic substances that influence their chemical reactivity: (1) polyfunctionality, the existence of a variety of functional groups and a broad range of functional reactivity, representative of a mixture of interacting heteropolymers (2) macromolecular charge, the development of polyelectrolyte character with the resultant effect on functional group reactivity and molecular conformation (3) hydrophilicity, the tendency to form strong hydrogen bonds with water molecules solvating polar functional groups and (4) structural lability, the capacity to associate intermolecularity and to change molecular confirmation in response to changes in pH, pE values, electrolyte concentration, and functional group binding.

Humic substances provide important sources of both dissolved and colloidal organic ligands and therefore, can influence the bioavailability of trace metals in soils, sediments and aquatic systems. (Sposito, 1984; Tipping and Cooke, 1981; Davis and Bhatnagar, 1995) The interaction between a metal ion species and a humic substance is best classified as a "sorption reaction" varying from purely electrostatic to strongly covalent. (Sposito 1984). The bond that forms between the humic and metal species and surface functional groups is often not always clearly defined. Due to the polyfunctional nature of humics, the metal ion may attach to the ionized peripheral groups of the humic material or react with the functional groups creating inner-sphere and outer-sphere complexes.

Humic substances can sorb to mineral surfaces containing hydroxylated Al, Fe, or Mn sites thereby changing the mineral surface properties such as rendering the hydrophilic mineral surfaces hydrophobic, and more capable of sorbing metal species (Tipping and Cooke, 1982; Murphy et. al., 1990; and Zachara, 1994). Surface bound humic substances increase the adsorption of certain metal cations on single mineral solids by contributing additional, potentially high affinity, complexation sites. For metals forming strong complexes with humic substances, humic substances enhance metal ion binding to Fe and Al oxides at lower pH (e.g.,<6) by cosorption, but decrease metal ion sorption at higher pH by formation of nonsorbing aqueous complexes (Tipping et al.,1981; Tipping and Cooke, 1981; Davis and

Bhatnagar, 1995; and Murphy et. al., 1990). Consequently, particle-associated humic substances may form coatings on minerals, given that natural dissolved and colloidal organic material bind to a variety of oxide (Al and Fe) and layer silicate surfaces that are common in aquifers. (Tipping, 1981; Tipping and Cooke, 1982; Stumm, 1987; Murphy et al.,1992).

The structure of dissolved humic substances is largely determined by the groundwater pH, ionic strength, and the presence of divalent cations (Tipping, 1981; Tipping and Cooke, 1982; Christman and Gjessing, 1983; Murphy et. al., 1990; Murphy et. al., 1992) At high ionic strength, low pH, or in the presence of cations, the charge repulsion between adjacent carboxyl or hydroxyl groups on the humic substance is neutralized, resulting in a coiled configuration (Tipping and Cooke, 1982; Tsutsuki and Kawasuka, 1983) . At the mineral/solution interface the coiled configuration can result in fewer attachment points between the humic carboxyl and mineral surface hydroxyl groups and an extension of a shear plane outward from the mineral surface. Conversely, at low ionic strength, high pH and in the absence of cations, the humic substance may adopt a more open configuration in solution, resulting in more attachment points upon sorption to the mineral surface (Tipping and Cooke, 1982; Tsutsuki and Kawasuka; 1983; Murphy et al., 1992; Zachara et.al., 1994).

The humic material is susceptible to configuration changes with different ionic strength buffer. Reagents such as perchlorates and phosphates for example, have an effect on the sorptive behavior of the humic material to the aquifer solids. In some cases, the buffering solution may be involved in direct competition with the humic materials for specific sites on the aquifer material. It is believed that phosphates (PO_4^-) compete directly with the humic material for the Al-OH and Fe-OH sites. The extent of composition on the physical properties of the aquifer material and the concentration of the buffer itself. (Tipping, 1981; Tipping and Cooke, 1982; Tsutsuki and Kawasuka, 1983; Murphy et. al., 1992).

Published data for humic substance sorption onto mineral surfaces suggest that sorption tends to follow a Langmuir-type isotherm curve fit (Tipping, 1981; Murphy et. al., 1990). The Langmuir isotherm is based on the concept that a solid surface poses a finite number of sorption sites. When all the sorption sites are filled, the surface will no longer sorb solute from solution thus a sorption plateau is reached when all sites are filled (Fetter, 1993). The form of the Langmuir sorption isotherm is:

$$C/C^* = 1/\alpha\beta + C/\beta$$

where:

C = initial amount substance present

C^* = amount of material sorbed at the end of reaction

α = an absorption constant related to the binding energy (l/mg)

β = the maximum amount of solute that can be absorbed by the solid (mg/kg)

If C/C^* is plotted versus C, the data will be linear with maximum ion sorption, β, as the reciprocal of the slope of the line and the binding energy constant, α, as the slope of the line divided by the intercept.

A more general or true equilibrium isotherm is the Freundlich sorption isotherm. This is defined by the nonlinear relationship:

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$$C^* = KC^N$$

where K and N are constants.

If the sorption characteristics can be described by a Freundlich sorption isotherm, where C is plotted as a function C*, the data will be curvilinear. However, the data can be linearized by log transformation by the use of the following equation:

$$\log C^* = \log K + N \log C$$

When log C is plotted against C*, the result will be linear with a slope of N and an intercept of log K. When the linear intercept (constant N) is equal to 1, the linear isotherm is obtained.

Little is known about the chemical and physical properties of the mineral-bound organic coatings and their potential influence on humic acid sorption to low-carbon sediments. Numerous studies, such as the ones referred to previously, have studied sorption onto well characterized clays and minerals. Natural are a complex matrix of minerals with heterogeneous surfaces on which sorption may occur. The objective of this study to develop a better understanding of the sorptive capacity of natural aquifer materials for humic compounds. This information is necessary to understand the fate and transport of humics in natural aquifer systems so that future sorption studies with metals and other contaminants known to bind to humics can be more clearly understood. This study examined the sorption of humic acids to aquifer materials. Two well characterized standard humics were sorbed to three well characterized aquifer materials. The effects of concentration, pH and ionic strength was studied.

Materials

Sediments:

Aquifer solid materials used consisted of unconsolidated sediments from aquifers at Columbus AFB, Mississippi, Barksdale AFB, Louisiana and Blytheville AFB, Arkansas. The sediments were provided by Dr. T. Stauffer and their collection and treatment are presented in Stauffer (1987) and Libelo (1995) and summarized in Table 1.

Humic Acids:

Two humic acid materials were used in this study, a readily available commercial product, and a well characterized standard material obtained from the International Humic Substances Society (IHSS.) The humic material used for the primary sorption study was Aldrich Humic Acid, Sodium Salt (Aldrich Co., Germany). Aldrich estimated the molecular weight range of their humic material between 5,000 - 500,000 daltons. It has a black, powdery consistency and is quite water soluble..In water, the solutions are deep orange to yellow in appearance dependent on concentrations. (Kim et. al., 1990)

The IHSS humic substance used was Suwannee River Humic Acid Reference 1R101H (100mg.) it was obtained from Dr. P. MacCarthy at Colorado School of Mines. Suwannee River humic acid was isolated from the Suwannee River in Florida which drains the Okefenokee River in southern Georgia. It is a light brown compound, highly water soluble and has a characteristic yellow to pale color in solution depending on concentration. See Table I for physical properties of the humic acids used.

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Methods

Rationale for Chosen Methodology and Conditions:

Batch equilibration technique was used to measure sorption of humic acids to aquifer material solids because it 1) allows for the determination of an entire sorption isotherm in a short amount of time, 2.) is commonly used in similar studies of surface soil and sediments, and involves fewer variables than dynamic (column) techniques (Stauffer, 1987).

Sorption Studies at Varying pH:

The humic material used for the preliminary sorption study was the commercial Humic Acid, Sodium Salt obtained form Aldrich Co. A series of 10-fold dilutions from a 1000 mg/L solution were prepared, and a calibration curve was generated as in Davis and Bhatnagar (1995) in order to establish absorbance and concentration parameters. The dissolved humic acid concentration was determined by measuring absorbance at 240 NM using a Carey 3E UV-Visible Spectrophotometer (Varian Instruments) with quartz cuvettes. All isotherm experiments were conducted using 18 OHM Milli-Q water (Millipore Co.) in order to minimize organic and inorganic contaminants. No attempt in this phase of the experiment was made to produce a "synthetic" groundwater by adding inorganic salts or buffers to the Milli-Q water, since each groundwater sample is a product of the particular geologic materials through which it passes and no standardized formula can be made.(Stauffer (1987). The sorption experiments at varying pH were conducted in the absence of buffer solutions. Ionic strength studies did however vary ionic strength buffers and concentrations and was done in a later, independent portion of this study.

Humic Acid Solutions:

Physical characteristics from Table II of the humic materials used in our studies indicates that carbon makes up 49-51% of each sample. The total organic carbon content of natural waters ranges from 1 to 30 mg C/L (Aiken et al. 1985), this experiment utilized concentrations several orders of magnitude above the average in all varying pH isotherm experiments in order to properly study the effects of a range of concentrations of humic acid; from nominal 25-1000 mg.C/L. Each set ranged from nominal 1000 mg/L humic acid ($\approx$350-425 mg C /L) to 25 mg/L ($\approx$11-13 mg C /L). For the IHSS Suwannee humic acid, quantities were limited and so sorption studies were conducted with lower concentrations i.e. ranging from 100 mg/L ($\approx$39-54 mg C/L) to 25 mg/L ($\approx$11-13 mg C/L)

The sample preparation at a given pH on each sediment was conducted in the following manner: The humic acid standards were brought to the appropriate dilution mark with Milli-Q water, stirred at room temperature (22.5^{0}C +/- 1^{0}C) for one hour, purged with N_2 for approximately 20 minutes and then poured into sterile disposable Nalgene® containers for pH determination. The pH values were measured using an Accumet® Model 25 (Fisher-Scientific) instrument equipped with a silver/silver chloride electrode. All pH readings are (+/- 0.1) unit based on manufacturer specifications. The pH of the humic standards was

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adjusted by drop-wise additions of concentrated HCl and NaOH (Fisher Co.) respectively. The pH values varied from 1-2 units during the experiment as a result of the natural buffering capacity of the aquifer solid.

A fixed sorbate-solution ratio of 1 gm : 2.5 mL was maintained throughout. The sorbate-solution separations by centrifugation were made as complete as possible to avoid possible sorbate concentration effects. Differences in sorbent density caused the solid-liquid ratio to vary somewhat because the same containers (constant total volume) were used in all isotherm experiments. All data acquired on different sorbents within this work are comparable with regard to solid-liquid ratio.

Aquifer Solids:

The reaction vials were prepared in the following manner: 1 gram (+/- .0005 gm.) of each aquifer solid was weighed into a clear borosilicate, serum bottle (Aldrich Co.) using a Mettler AE 160 analytical balance. Sorption of humic solutions with the serum vial was not significant, ranging from 0.9-2% over a period of 72 hours. The humic acid solution was pipetted onto the sediment. The vials were then capped with butyl rubber stoppers and crimp sealed under an N_2 environment. The vials were placed on a rotary shaker table (Lab-Line, Melrose Park IL) and shaken at 100 RPM for 24 hours. Samples were then centrifuged (Damon/IEC EPR-6000) at 2,500 g. for 25 minutes. The supernatant was then used for total organic carbon (TOC) analysis. The total organic carbon present in each sample was quantified using a combustion/non-disperse infrared gas analysis system; (Shimadzu TOC-5000 coupled to a Shimadzu ASI-5000 autosampler, Shimadzu Corp.,Japan) The amount of humic material sorbed onto the sediment was determined by difference from sediment-free samples. The sampling done was batch-process type, with each vial prepared in triplicate,

Ionic Strength Measurements

The procedures employed in this portion of the experiment paralleled those for the non-buffered pH isotherm experiments. However, the study was conducted only on Columbus AFB sediment with Aldrich humic acid because its abundance and, with respect to Barksdale and Blytheville, demonstrated higher sorptivity of the humic material. Two anionic sodium buffers were used ; sodium perchlorate $NaClO_4$ (Aldrich) and Sodium phosphate monohydrate $NaH_2PO_4 \cdot H_2O$ (Fisher). Two concentrations were prepared using each buffer, 0.1M and 0.005 M. The buffer solutions were prepared with Milli-Q water and had a pH upon dilution of 6.7 for the sodium perchlorate and 4.2 for sodium phosphate monohydrate. The solutions were then brought to pH 7(+/-0.1) by drop-wise addition of dilute HCl and or NaOH,. allowed to equilibrate at room temperature for one hour, and then used to prepare the humic acid standards in the same manner as in the pH studies. Slight pH variations occurred when humic acid standards were prepared with the sodium buffer solutions requiring addition of acid or base to obtain the necessary pH. After equilibration, 5 mL of solution aliquots were pipetted into vials containing 2 gm. of aquifer material. The samples were then crimp sealed under an N_2 environment, shaken for 24 hours and

centrifuged for 20 minutes at 20,000 g. The supernatant was then analyzed for TOC sorption; determined by difference from sediment-free blanks.

Results and Discussion

The observed trend of TOC sorbed as a function of humic concentration, over all pH ranges was; Columbus > Blytheville > Barksdale. Figures 1-3 of this report represent the isotherms encompassing the nominal pH range 4-7(+/- 0.1 units). The extent of sorption of humic acid substances to three different aquifer material solids decreases with increasing pH. In addition, the sorption constants (K_d) decreased with increasing pH for all sediments; Columbus 2.321 - 0.352, Barksdale 0.323 - 0.079 and Blytheville 0.574 - 0.113. A similar pH dependence was found by Tipping (1981) for the sorption of Esthwaite water humic substances to hydrous iron oxides and by Murphy et al. (1992) for the sorption of various IHSS humic and fulvic acids onto hematite and kaolinite. In contrast to the previously mentioned studies, our study utilized natural aquifer materials. Each type of aquifer solid was extracted from three separate locations from Air Force bases around the southern portion of the United States. Consequently, our samples not only differ in geographical origins but in their physical properties as well. The isotherm plots illustrated in Figures 1-3 of this report show that our low-carbon aquifer sediments behaved similarly to the well classified clay materials of past studies and the results are very much in line with those of the past works mentioned above.

The pH values depicted on the isotherm plots reflect the pH values determined following the 24 hour equilibration time. It should be pointed out that the pH values did not remain at their nominal values, as a result of the sediments natural buffering capacity. For Barksdale and Blytheville sediments, the pH changed 2-3 units from the starting values as compared to a 0.8 - 1 pH unit change for the Columbus sediment. The final pH value range after equilibration for Barksdale was 6.79 - 8.03, for Blytheville and Columbus sediments the ranges were 6.57- 7.98 and 4.83 - 7.79 respectively. This buffering capacity most likely is the result of carbonate, or phosphate species on the aquifer sediments most likely from the clay minerals.

The physical properties of the aquifer materials (Table 1), may correlate with the observed trend seen with pH variation. Columbus AFB sediment sorbed the highest amount of TOC, (29-80% at pH 4) of the humic material added. Columbus sediment has a considerable surface area (5.74 m^2/gm) and surface iron composition (0.914 g/kg). In addition, Columbus sediments are about 70.8% sand. Conversely, Columbus is made up of a significant percentage of silt and clay; 17.50% and 11.68% respectively. This suggests that it is the sites on the silt and clay that are most likely involved in the sorption of the humic material. They contain the surface hydroxyl sites involved in surface metal oxide interaction and ligand exchange mechanisms. This is further illustrated by comparison of the physical properties of Blytheville sediment sorption isotherms. Although Blytheville has the largest surface area, (9.32 m^2/g), and dithionite iron composition, (1.64 g/kg) of the three sediments studied, it is comprised of a substantial percentage of sand, 95.6% and subsequently a rather small percentages of silt and clay; 3.06% and

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1.34% respectively. Sand does not provide sites where sorption may occur, consequently both Blytheville and Barksdale aquifer sediments sorbed only 2-30% (at pH 4) of the humic acid in solution at equilibrium less than Columbus. This can be attributed to their low percentages of clay and silt compositions, resulting in fewer sites for sorption.

Several explanations regarding the effect of pH variation on humic sorption could assist in explaining the observed trend. Primarily, the sorption of humic substances increases with decreasing pH in response to positive charge development on the sorbents (Tipping, 1981). Protons may neutralize the negative charges on humic anionic groups. not involved in the adsorptive interaction, and decrease electrostatic repulsion when the HS concentrates at the interface. (Tipping, 1981; Tipping and Cooke; 1982). In addition this observation is consistent with a ligand exchange mechanism previously suggested by Tipping, 1981; Tipping and Cooke, 1982; Davis, 1982; and Murphy et al., 1992. Sorption of humic substances by ligand exchange is believed to occur in the following sequence (Sposito, 1984):

(1) $SOH + H^+ <=> SOH_2^+$

(2) $SOH_2^+ + HuC(O)O^- <=> SOH_2^+ -OC(O)-Hu$

(3) $SOH_2^+ -O-C(O)-Hu <=> SO-C(O)-Hu + H_2O$

SOH represents the surface hydroxyl group on the sorbent, and $HuC(O)O^-$ represents the humic carboxyl group. Equation (1) represents the protonation step believed to render the surface hydroxyl group more exchangeable (Sposito, 1984). The protonation step is responsible in part, for the pH dependence of the fractional sorption. Equation (2) represents the formation of the humic carboxyl group, an outer-sphere surface complex with a protonated hydroxyl group. Equation (3) represents ligand exchange (OH_2 for Hu-COO-) that is postulated to occur.

The second humic acid was sorbed onto these aquifer sediments to determine if a different type of humic acid would behave differently than the commercial non-purified Aldrich humic material. The results of Murphy et al. (1992) point out that the sorption of humic substances was directly proportional to the aromaticity and inversely proportional to the polarity as approximated by the elemental O/C ratio. Table 2 compares some of the physical properties of the Aldrich and Suwannee humic acid. The percent aromaticity and O/C ratios of Aldrich and Suwannee River humics are comparable. Accordingly, sorption isotherms (Figures 7 and 8) show that sorptions are quite comparable. The isotherms satisfactorily depict the initial, linear portion of the isotherm. It is clear that these isotherms are in reasonably good agreement with the conclusions of Murphy et.al., (1990) that O/C ratios and percent aromaticity are the key factors which govern humic acid sorption. Table 4 illustrates the results of the statistical treatments for the sorption of Aldrich and Suwannee humic acid on to Barksdale and Blytheville sediment.

The data for the isotherm plots of Figures 1-3, 7 and 8 were treated by statistical methods to determine the best fit parameters to our data values. Tipping (1981) and Murphy et. al. (1992) determined that Langmuir fits were the most statistically favorable in the treatment of their data. However, as pointed out by Stauffer (1987), the choice of statistical methods applied to humic acid sorption is often varied and no mathematical treatment of the data is uniformly accepted as better than

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another. In this study, the sorption data were fit to Linear, Langmuir and Freundlich isotherms to determine the best statistical fit. Figures 4-6 illustrate the different isotherm fits for Aldrich humic acid at nominal pH = 4. Linear and Freundlich isotherm plots fit our data better than the Langmuir fits. This may be attributed to the fact that our natural sediment surfaces are heterogeneous rather than well defined homogeneous clays and minerals used by Tipping (1981) and Murphy et al.(1990). The linear K_d and Freundlich log K (intercept) and N (slope) are shown in Tables 3, 4 and 5.

Two different ionic strength studies were conducted using two compounds with distinctively different chemical properties and known effects on humic acid sorption. The compounds used were sodium perchlorate (NaClO$_4$ and sodium phosphate monobasic (NaH$_2$PO$_4$•H2O). The results of the ionic strength isotherms were consistent with those found by Tipping(1981); Tipping and Cooke (1982); Tsutsuki and Kuwatsuka (1981) and Murphy et. Al. (1992). Figure 9 of this report illustrates the effects of each buffer at high and low ionic strength; 0.1 M and 0.005 M respectively. As pointed out in the introduction, ionic strength and pH variation have an effect on the functional groups of the humic acids. These functional group changes thereby alter the sorptive capacity of the humic acid onto the aquifer material solid. The aquifer material used in this study was Columbus AFB solids. This particular aquifer material was selected because in comparison to Barksdale and Blytheville solids, Columbus sediments supported noticeable sorption and a complete isotherm could be followed readily within our detection limits.

Sodium perchlorate is a relatively strong oxidizing agent and has the capacity to maintain it's ClO$_4^-$ ion in solution. The results of the sodium perchlorate buffered humic acid isotherms appear to support the conclusions of the Murphy et al., (1992) that humic acids seem to adopt a more linear or open configuration at low ionic strength, and on a mole carbon basis, occupy a greater amount of mineral surface than humic acids at high ionic strength. In addition, our results supported the findings of Tsutsuki and Kuwatsuka (1984) which stated that the humic acid molecule is fully expanded at low ionic strength at pH 7.5, but folds onto itself considerably with increasing ionic strength. Due to the fact that the humic acid tends change its structural configuration, it subsequently may have less exposed ionizable carboxyl and hydroxyl sites available for sorption onto the sediment. For reference purposes, the isotherm of a non-buffered humic acid solution is plotted in Figure 9, and as is evident, the amount of TOC sorbed is quite a bit less ≈35-40% then in the 0.1 M perchlorate-buffered isotherm.

Tipping (1981) pointed out that in some instances, the presence of certain anion species like phosphates (PO$_4^-$) can effect the sorption of humic acids onto iron oxide materials because they directly compete with the humic acid for the surface hydroxyl site on the sediment. As is depicted in Figure 9, the presence of the phosphate ion greatly reduces the TOC sorbed onto the natural aquifer material. Comparison of the TOC sorbed between 0.1 M and 0.005 M sodium phosphate demonstrate that the differences in concentration by a factor of 20 are not dramatic. This is most likely due to the fact that the phosphate loading capacity on the sediments has been achieved and excess phosphate may itself bind to a portion of the humic acid or remain in the colloidal suspension with the remainder of the humic acid.

The results are however notable when one compares the phosphate buffered isotherm to the non-buffered isotherm. The amount of TOC sorbed in the presence of phosphate ions is $\approx$ 26-48 % less than that seen in the phosphate-free reference isotherm. Most importantly, it is clear from this low TOC uptake that a competition for the aquifer site exists between the PO_4^- and the larger, more bulky humic material. This is the first study of whole sediments not specific minerals with phosphate species. This study not only gives a more accurate understanding of the interaction of natural aquifer materials with phosphates it gives a much better understanding of overall sorptive capacities of these natural materials.

Conclusions and Future Work

The results of this experiment will allow new insight into the sorption capacity of natural aquifer materials for humic acids under varying conditions of pH, concentration and buffer species. This information will be important for further sorption studies involving the use of additional sorptive species such as metals and environmental pollutants. Preliminary studies regarding the desorption of the humic materials from the sediments were conducted but need to be explored further. It will be important in future studies incorporate more humic and fulvic acids than the ones used here. In addition, more spectroscopic techniques such as atomic adsorption and fluorescence spectroscopy should be employed to further examine the role of Fe(II) and Fe(III) species whose presence is important for numerous environmental systems.

Figure 1.

Aldridch Humic Acid Sorption
onto Barksdale Aquifer Sediments
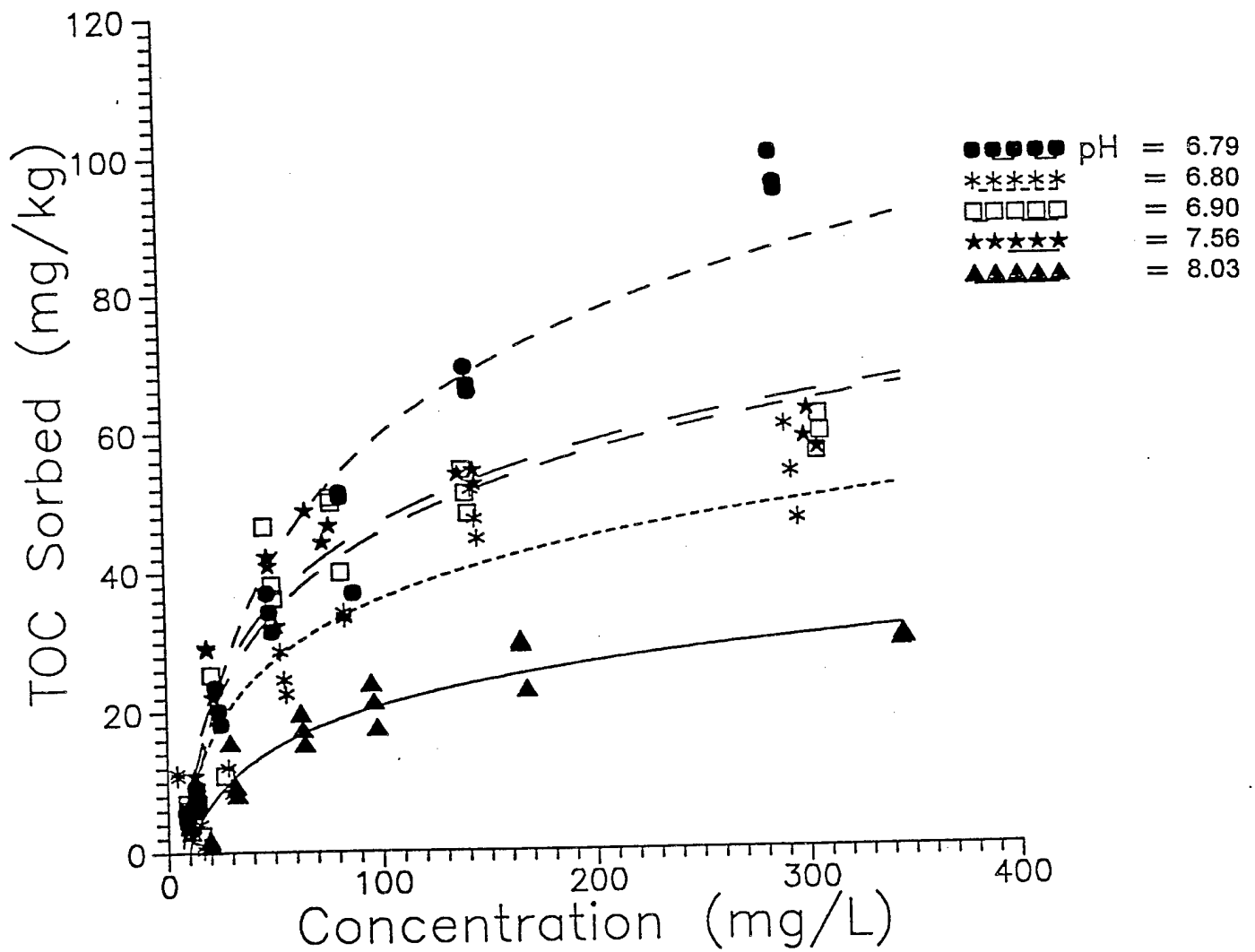
Figure 2.

Aldridch Humic Acid Sorption
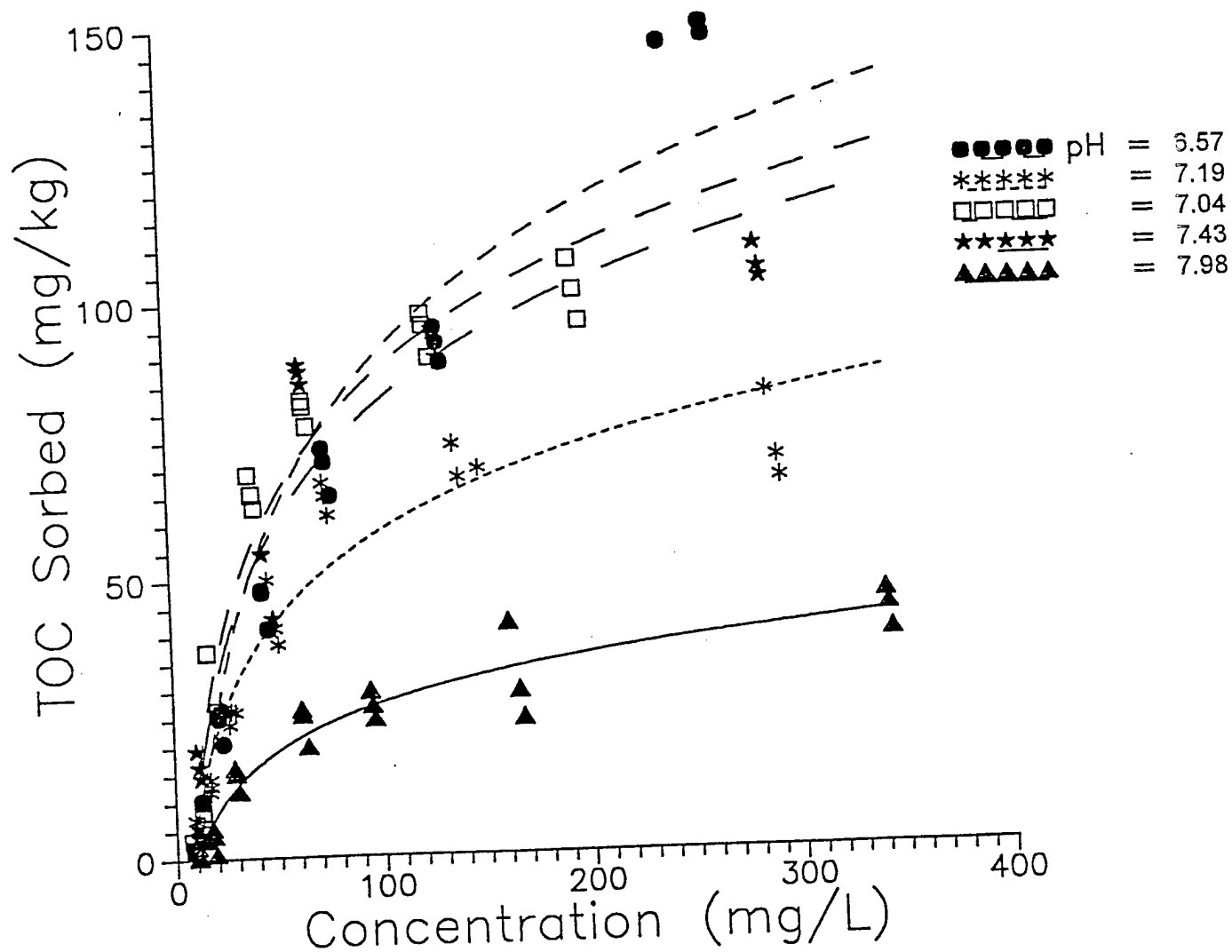onto Blytheville Aquifer Sediments

Figure 3.

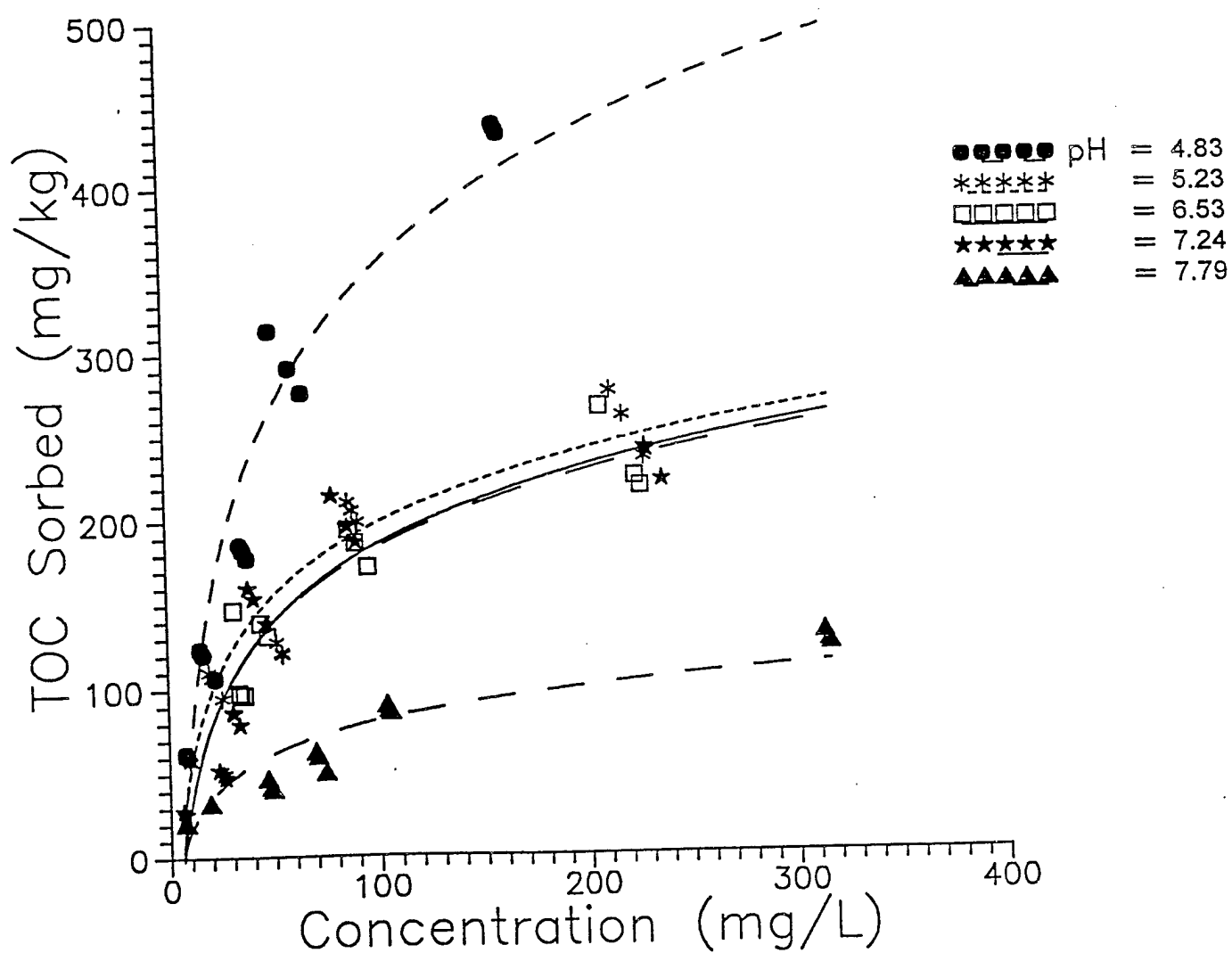Aldridch Humic Acid Sorption
onto Columbus Aquifer Solids

Figure 5.

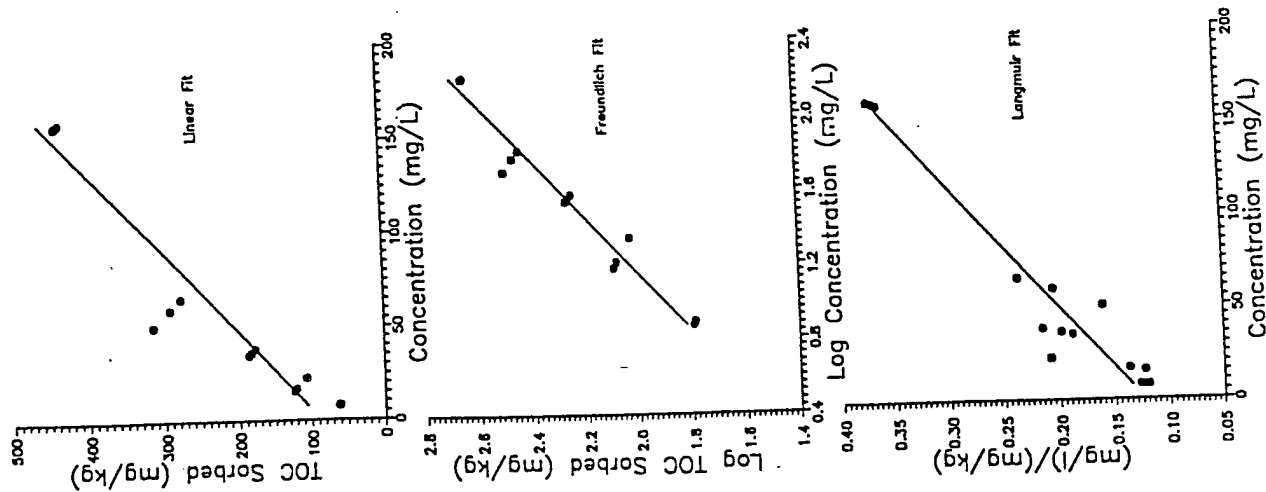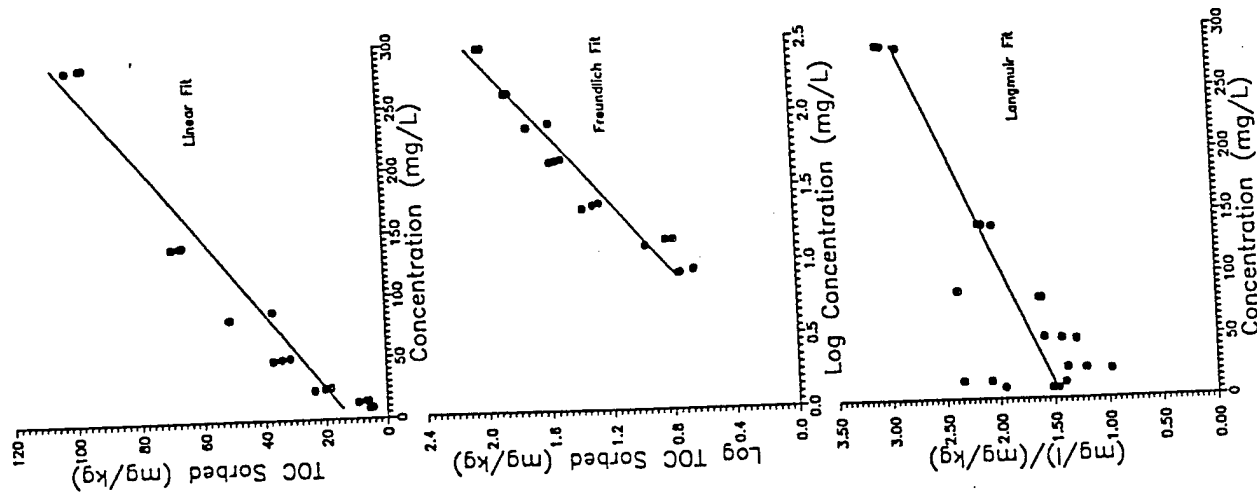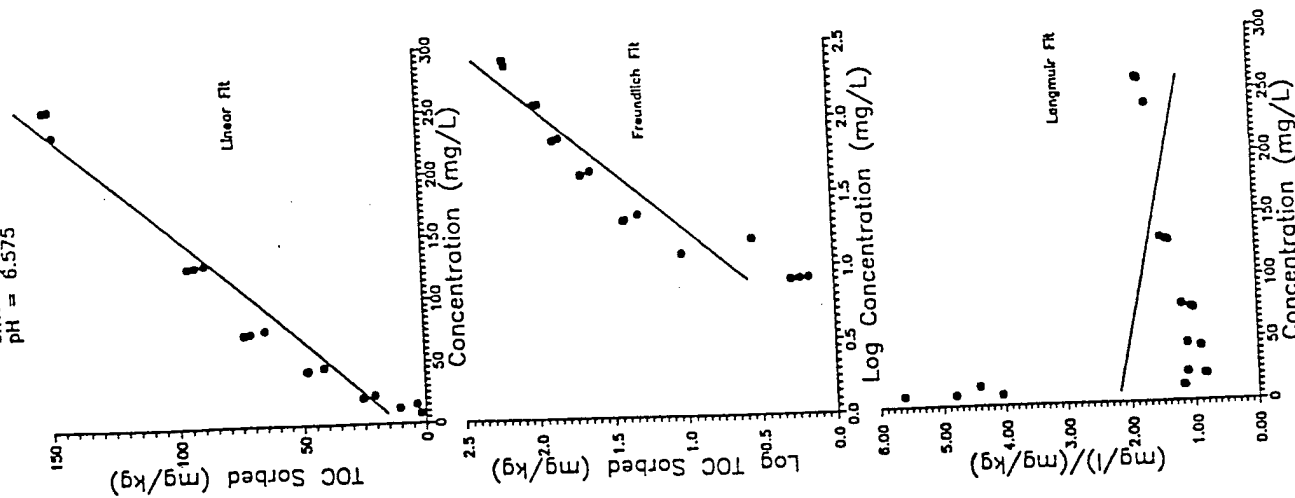Aldrich Humic Acid Sorption onto Blytheville Sediments
pH = 6.575

Aldrich Humic Acid Sorption onto Barksdale Sediments
pH = 6.792

Figure 4.
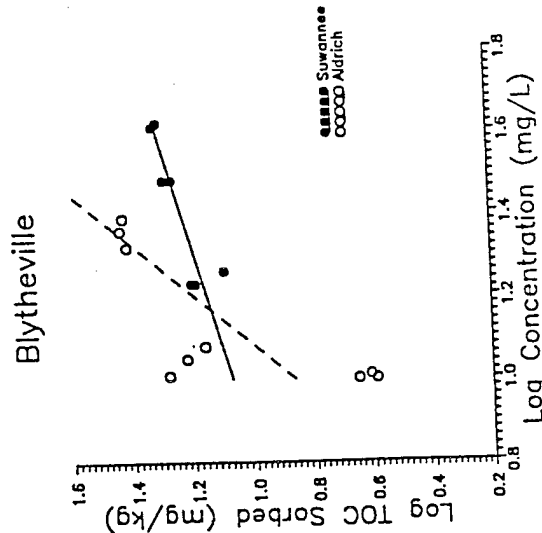
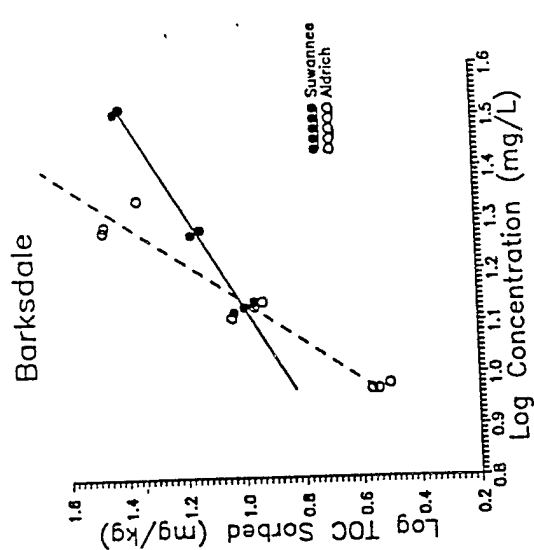Aldrich Humic Acid Sorption onto Columbus Sediments
pH = 4.83

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Figure 7.

Sorption of two humic acids on aquifer material solids. (Initial pH = 4)

(Initial pH = 7)
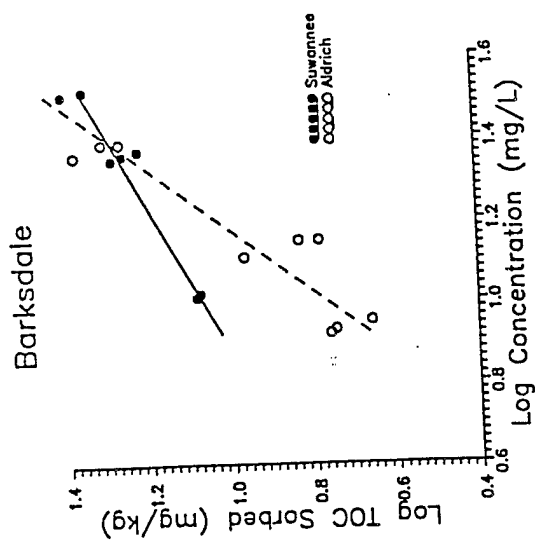

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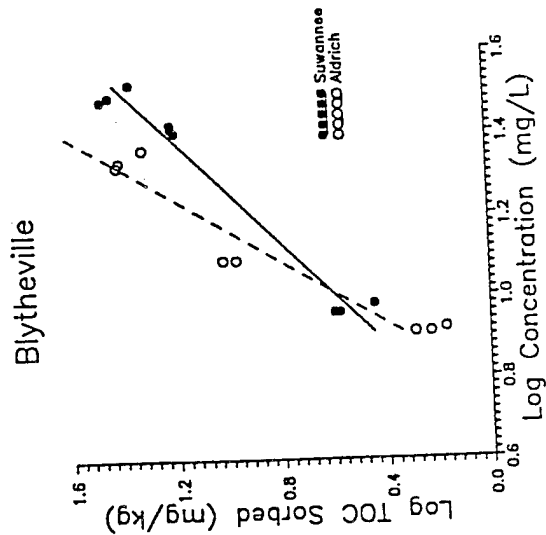
Figure 9.

Effect of ionic strength on sorption of
Aldrich humic acid onto Columbus
aquifer solids

Open symbol — sodium perchlorate
Closed symbol — sodium phosphate

●●●●● 0.005 M
▲▲▲▲▲ 0.1 M
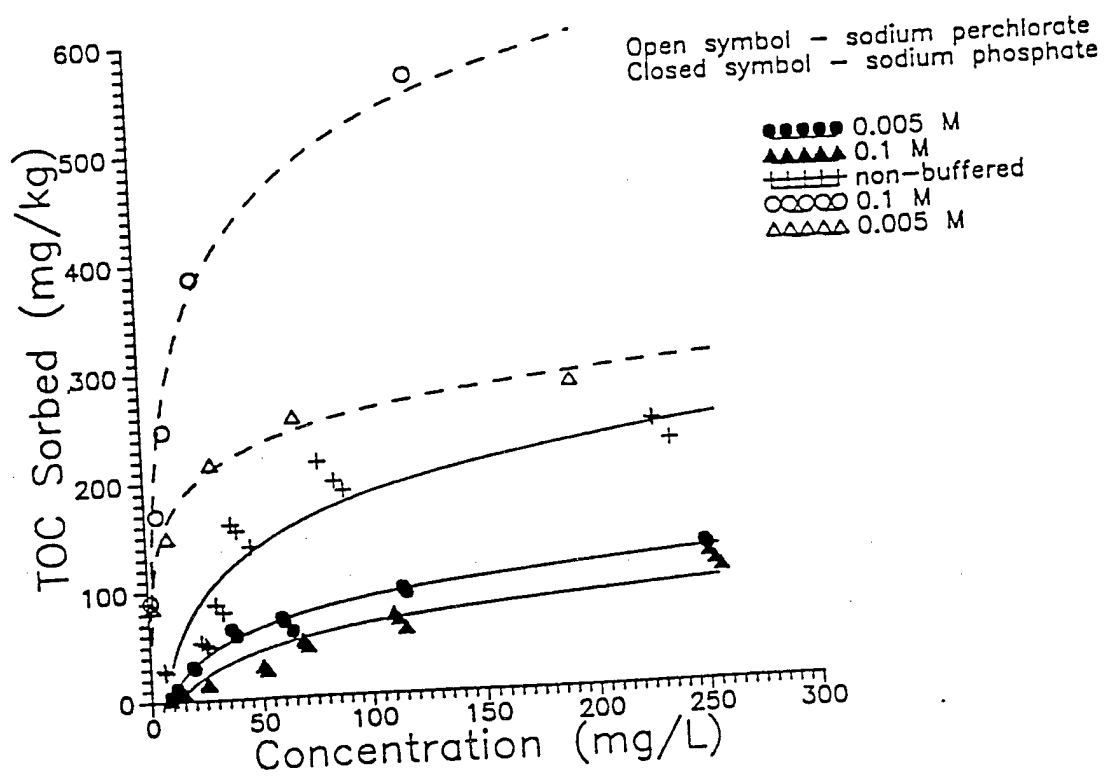╫╫╫╫╫ non—buffered
◯◯◯◯◯ 0.1 M
△△△△△ 0.005 M

Table 1. Chemical and Physical Characteristics of Aquifer Materials[1].

Aquifer	Total Organic Carbon % (sd) n = 5	Surface Area m²/g (sd) n = 5	Dithionate Iron g/kg (sd) n = 5	% Sand	% Silt	% Clay
Barksdale	0.0338 (0.0038)	0.88 (0.22)	0.112 (0.04)	96.1	1.94	1.97
Blytheville	0.0676 (0.0047)	9.32 (0.05)	1.64 (0.317)	95.6	3.06	1.34
Columbus	0.0596 (0.0062)	5.78 (0.049)	0.914 (0.067)	70.8	17.50	11.68

1. Libelo (1995)

Table 2.

Physical properties of the humic acids.

Sample	Elemental Composition						Atomic Ratios		Aromatic C (110-165)	Aliphatic C (0-90)	Carboxyl C (165-190) PPM
	C	H	N	S	O	Other	H/C	O/C			
Aldrich Humic Acid[a]	41.72	4.37	0.25	1.90	36.93	14.83	1.03	0.51	40	41	14
Suwannee River Humic[b,c] (1R1O1H)	50.50	3.35	1.18	0.55	44.42		1.26	0.66	37	28	19

a: Kim et al., 1990
b: Thurman and Malcolm, 1981
c: USGS Technical Report, 1989

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Table 3.

Isotherm results of Aldrich humic acid sorption on aquifer solids.

Sediment	pH[a]	Linear Fit $K_d{}^b$	Freundlich Fit log K	N
Columbus	4.83	2.321 (0.213)	1.251 (0.062)	0.649 (0.035)
	5.23	0.884 (0.104)	1.351 (0.06)	0.462 (0.033)
	6.53	0.641 (0.105)	1.426 (0.067)	0.411 (.061)
	7.24	0.846 (0.141)	0.918 (0.127)	0.664 (0.064)
	7.79	0.352 (0.028)	0.908 (0.050)	0.476 (0.016)
Barksdale	6.79	0.323 (0.021)	0.0041 (0.111)	0.846 (0.048)
	6.795	0.175 (0.021)	0.075 (0.445)	0.677 (0.174)
	6.908	0.164 (0.03)	0.149 (0.255)	0.726 (0.097)
	7.563	0.162 (0.029)	0.181 (0.224)	0.726 (0.096)
	8.03	0.079 (0.012)	-0.380 (0.257)	0.798 (0.014)
Blytheville	6.57	0.574 (0.031)	0.50 (0.247)	1.191 (0.107)
	7.19	0.222 (0.040)	0.231 (0.155)	0.747 (0.074)
	7.04	0.492 (0.069)	-0.12 (0.27)	1.035 (0.121)
	7.43	0.338 (0.055)	0.182 (0.231)	0.841 (0.101)
	7.98	0.113 (0.016)	-0.801 (0.349)	1.063 (0.151)

a: pH of supernatant after equillibration
b: Linear least-squares regression of data
( ) standard error of coefficient

Table 4

Isotherm results of Aldrich and Suwannee River humic acid sorption on aquifer solids.

Sediment	Humic Acid	pH[a]	Linear Fit K_d[b]	Freundlich Fit log K	N
Barksdale	Suwannee	4	0.480 (0.048)	6.7E-16 (1.5E-16)	1.0 (2.4E-16)
	Suwannee	7	0.807 (0.035)	-0.216 (0.028)	1.067 (0.060)
	Aldrich	4	0.996 (0.149)	-0.529 (.112)	1.298 (.2032)
	Aldrich	7	2.065 (0.323)	-1.985 (0.102)	2.608 (0.251)
Blytheville	Suwannee	4	0.936 (0.119)	-1.007 (0.078)	1.588 (0.113)
	Suwannee	7	0.236 (0.043)	-0.687 (0.037)	0.384 (0.079)
	Aldrich	4	1.554 (0.152)	-2.003 (0.174)	2.581 (0.331)
	Aldrich	7	1.307 (0.326)	-0.729 (0.260)	1.598 (0.544)

a: Initial pH of humic acid solution.
b: Linear least-squares regression of data.
( ) standard error of coefficient

Table 5.

Isotherm statistical sorption results of buffered humic acid solutions onto Columbus AFB aquifer solids.

Buffer	Ionic Strength	Linear Fit K_d	Freundlich Fit log K	N
Sodium Phosphate	0.005 M	0.461 (0.048)	-0.01 (0.238)	0.969 (0.105)
	0.1 M	0.439 (0.019)	-0.580 (0.162)	1.16 (0.074)
Sodium Perchlorate	0.005 M	0.819 (0.317)	1.917 (0.357)	0.258 (0.027)
	0.1 M	3.248 (0.904)	1.937 (0.059)	0.415 (0.041)
Non-Buffered		1.273 (0.15)	0.918 (0.128)	0.664 (0.064)

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